

Information Entropy, Information Distances and Complexity in Atoms

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Abstract

Shannon information entropies in position and momentum spaces and their sum are calculated as functions of Z ($2 \leq Z \leq 54$) in atoms. Roothaan-Hartree-Fock electron wave functions are used. The universal property $S = a + b \ln Z$ is verified. In addition, we calculate the Kullback-Leibler relative entropy, the Jensen-Shannon divergence, Onicescu's information energy and a complexity measure recently proposed. Shell effects at closed shells atoms are observed. The complexity measure shows local minima at the closed shells atoms indicating that for the above atoms complexity decreases with respect to neighboring atoms. It is seen that complexity fluctuates around an average value, indicating that the atom cannot grow in complexity as Z increases. Onicescu's information energy is correlated with the ionization potential. Kullback distance and Jensen-Shannon distance are employed to compare Roothaan-Hartree-Fock density distributions with other densities of previous works.

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I. INTRODUCTION

Information-theoretic properties are used in recent years for the study of quantum mechanical systems [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. In the present work we carry out a systematic study of Shannon information S , Onicescu information energy E , order parameter Ω and complexity $\Gamma_{\alpha,\beta}$, in atoms with $Z = 2 - 54$. In previous work [5] we proposed a universal property of S for density distributions of nuclei, electrons in atoms and valence electrons in atomic clusters. This property has the form

$$S = a + b \ln N \quad (1)$$

where N is the number of particles of the system and the parameters a and b depend on the system under consideration. Recently [4] we have obtained the same form for systems of correlated bosons in a trap. In the present paper we employ very accurate spin-independent atomic wave functions obtained by Bunge et al [19], by applying the Roothaan-Hartree-Fock method (RHF) to calculate analytical self consistent-field atomic wave functions. Thus we verify the above relation for atoms, which was obtained in the past [7, 8] employing another set of electron wave functions. Thus we obtain a framework to be used as a basis for further work on information-theoretic properties of atoms. An interesting question is the effect of the electron-electron correlations on S and relation (1), which could be answered in future research.

We focus our attention on the problem of similarity index based on the concept of an information distance. The concept of similarity is an old one and related to the distinction between two or more objects [20]. Specifically, in our paper we study two candidates connected with the concept of similarity or information distance. The first one is the Kullback-Leibler relative entropy K (and also the symmetrized Kullback distance SK) and the second one is the Jensen Shannon divergence J . Thus we are able to compare various density distributions obtained using various models. It turns out that S , SK and J measures are useful for this purpose.

The framework developed in the present work for S together with S_{max} obtained previously [8] with rigorous inequalities holding for S , S_r , S_k enables us to calculate the so called complexity measure $\Gamma_{\alpha,\beta}$ introduced in [21]. Our procedure leads to the interesting result that complexity as function of Z shows shell effects at closed shells atoms i.e. for the above atoms complexity decreases with respect to neighboring atoms.

The outline of our paper is the following: In Sec. II we describe measures of information content of a quantum system together with information distances of two probability distributions and a complexity measure recently proposed. In Sec. III we present our formalism, while Sec. IV contains our numerical results and discussion. Sec. V is a summary of the paper. Finally Sec. VI contains our comments on the importance of our results on complexity.

II. MEASURES OF INFORMATION CONTENT AND INFORMATION DISTANCES

The Shannon information entropy [22] S_r in position-space may be defined as

$$S_r = - \int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} \quad (2)$$

where $\rho(\mathbf{r})$ is the electron density distribution normalized to unity. The corresponding information entropy S_k in the momentum space representation is

$$S_k = - \int n(\mathbf{k}) \ln n(\mathbf{k}) d\mathbf{k} \quad (3)$$

where $n(\mathbf{k})$ is the momentum density distribution normalized to unity studied in [7, 23, 24, 25]. In position-space S_r determines the extent of electron delocalization, since it tends to a maximum as the distribution flattens out and deviates from this maximum when structure is introduced in $\rho(\mathbf{r})$. In momentum-space a maximum in S_k corresponds to a delocalized distribution in momentum-space [26]. The total information entropy is given by

$$S = S_r + S_k \quad (4)$$

where S , S_r and S_k obey the following rigorous inequalities [8]

$$S_{r\min} \leq S_r \leq S_{r\max} \quad (5)$$

$$S_{k\min} \leq S_k \leq S_{k\max} \quad (6)$$

$$S_{\min} \leq S \leq S_{\max} \quad (7)$$

The lower and the upper limits can be written, for density distributions normalized to

one

$$\begin{aligned} S_{r\min} &= \frac{3}{2}(1 + \ln \pi) - \frac{3}{2} \ln \left(\frac{4}{3} T \right) \\ S_{r\max} &= \frac{3}{2}(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{2}{3} \langle r^2 \rangle \right) \end{aligned} \quad (8)$$

$$\begin{aligned} S_{k\min} &= \frac{3}{2}(1 + \ln \pi) - \frac{3}{2} \ln \left(\frac{2}{3} \langle r^2 \rangle \right) \\ S_{k\max} &= \frac{3}{2}(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{4}{3} T \right) \end{aligned} \quad (9)$$

$$\begin{aligned} S_{\min} &= 3(1 + \ln \pi) \\ S_{\max} &= 3(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{8}{9} \langle r^2 \rangle T \right) \end{aligned} \quad (10)$$

where $\langle r^2 \rangle$ is the mean square radius and T is the kinetic energy.

Another measure of information content of a quantum system is the concept of information energy E introduced by Onicescu in an attempt to define a finer measure of dispersion distribution than that of Shannon information entropy [27]. For a discrete probability distribution (p_1, p_2, \dots, p_k) , E is defined as

$$E = \sum_{i=1}^k p_i^2 \quad (11)$$

which is extended for a continuous density distribution $\rho(x)$ as

$$E = \int \rho^2(x) dx \quad (12)$$

So far, only the mathematical aspects of the concept have been developed, while the physical aspects have been ignored. A recent study of E for atomic nuclei has been carried out in [28].

The meaning of (12) can be seen by the following simple argument: For a Gaussian distribution of mean value μ , standard deviation σ and normalized density

$$\rho(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right] \quad (13)$$

relation (12) gives

$$E = \frac{1}{2\pi\sigma^2} \int_{-\infty}^{\infty} \exp \left[-\frac{(x - \mu)^2}{\sigma^2} \right] dx = \frac{1}{2\sigma\sqrt{\pi}} \quad (14)$$

E is maximum if one of the p_i 's equals 1 and all the others are equal to zero i.e. $E_{max} = 1$, while E is minimum when $p_1 = p_2 = \dots = p_k = \frac{1}{k}$, hence $E_{min} = \frac{1}{k}$ (total disorder). The fact that E becomes minimum for equal probabilities (total disorder), by analogy with thermodynamics, it has been called information energy, although it does not have the dimension of energy [29].

It is seen from (14) that the greater the information energy, the more concentrated is the probability distribution, while the information content decreases. Thus one can define a measure of information content analogous to Shannon's S by the relation

$$O = \frac{1}{E} \quad (15)$$

Relation (12) is extended for a 3-dimensional spherically symmetric density distribution $\rho(r)$:

$$\begin{aligned} E_r &= \int_0^\infty \rho^2(r) 4\pi r^2 dr \\ E_k &= \int_0^\infty n^2(k) 4\pi k^2 dk \end{aligned} \quad (16)$$

in position and momentum space respectively, where $n(k)$ is the corresponding density distribution in momentum space.

E_r has dimension of inverse volume, while E_k of volume. Thus the product $E_r E_k$ is dimensionless and can serve as a measure of concentration (or information content) of a quantum system. It is also seen from (14) that E increases as σ decreases (or concentration increases) and Shannon's information entropy (or uncertainty) S decreases. Thus S and E are reciprocal. In order to be able to compare them, we redefine the quantity O by

$$O = \frac{1}{E_r E_k} \quad (17)$$

as a measure of the information content of a quantum system in both position and momentum spaces.

Landsberg [30] defined the order parameter Ω (or disorder Δ) as

$$\Omega = 1 - \Delta = 1 - \frac{S}{S_{max}} \quad (18)$$

where S is the information entropy (actual) of the system and S_{max} the maximum entropy accessible to the system. Thus the concepts of entropy and disorder are decoupled and it

is possible for the entropy and order to increase simultaneously. It is noted that $\Omega = 1$ corresponds to perfect order and predictability, while $\Omega = 0$ means complete disorder and randomness.

In [21] a measure of complexity $\Gamma_{\alpha,\beta}$ was defined of the form

$$\Gamma_{\alpha,\beta} = \Delta^\alpha \Omega^\beta = \Delta^\alpha (1 - \Delta)^\beta = \Omega^\beta (1 - \Omega)^\alpha \quad (19)$$

which is called the "simple complexity of disorder strength α and order strength β ". When $\beta = 0$ and $\alpha > 0$ "complexity" is an increasing function of "disorder", and we have a measure of category I (Fig.1 of [21]). When $\alpha = 0$ and $\beta > 0$, "complexity" is an increasing function of "order" and we have a measure of category III. When both α and β are nonvanishing and positive ($\alpha > 0, \beta > 0$), "complexity" vanishes at zero "disorder" and zero "order" and has a maximum of

$$(\Gamma_{\alpha,\beta})_{max} = \alpha^\alpha \beta^\beta / (\alpha + \beta)^{(\alpha+\beta)} \quad (20)$$

at $\Delta = \alpha/(\alpha + \beta)$ and $\Omega = \beta/(\alpha + \beta)$. This is complexity of category II according to [21].

Several cases for both α and β non-negative are shown in fig.2 of [21] where $\Gamma_{\alpha,\beta}$ is plotted as function of Δ . In the present work we can find $\Delta = S/S_{max}$ or $\Omega = 1 - \Delta$ as function of Z . Thus we are able to plot the dependence of $\Gamma_{\alpha,\beta}$ on the atomic number Z .

The Kullback-Leibler relative information entropy K [31] for any probability distributions $p_i^{(1)}, p_i^{(2)}$ is defined by

$$K(p_i^{(1)}, p_i^{(2)}) = \sum_i p_i^{(1)} \ln \frac{p_i^{(1)}}{p_i^{(2)}} \quad (21)$$

which for continuous probability distributions is defined as

$$K = \int \rho^{(1)}(x) \ln \frac{\rho^{(1)}(x)}{\rho^{(2)}(x)} dx \quad (22)$$

(21), (22) can be easily extended for 3-dimensional systems. K measures the difference of distance of $\rho_i^{(1)}$ from the reference (or a priori) distribution $\rho_i^{(2)}$.

It satisfies: $K \geq 0$ for any distributions $\rho_i^{(1)}, \rho_i^{(2)}$. It is a measure which quantifies the distinguishability (or distance) of $\rho_i^{(1)}$ from $\rho_i^{(2)}$, employing a well-known concept in standard information theory. In other words it describes how close is $\rho_i^{(1)}$ to $\rho_i^{(2)}$ by carrying out observations or coin tossing, namely trials L (in the sense described in [32]).

However, the distance K does not satisfy the triangle inequality and in addition is i) not symmetric ii) unbounded and iii) not always well defined [32]. To avoid these difficulties Rao

and Lin [33, 34] introduced a symmetrized version of K [32], the Jensen-Shannon divergence

$$J(\rho^{(1)}, \rho^{(2)}) = H\left(\frac{\rho^{(1)} + \rho^{(2)}}{2}\right) - \frac{1}{2}H(\rho^{(1)}) - \frac{1}{2}H(\rho^{(2)}) \quad (23)$$

where $H(\rho) = -\sum_i \rho_i \ln \rho_i$ stands for Shannon's entropy. J is minimum for $\rho^{(1)} = \rho^{(2)}$ and maximum when $\rho^{(1)}$ and $\rho^{(2)}$ are two distinct distributions, when $J = \ln 2$. In our case J can be easily generalized for continuous density distributions. For J minimum the two states represented by $\rho^{(1)}$ and $\rho^{(2)}$ are completely indistinguishable, while for J maximum they are completely distinguishable. The amount of distinguishability can be further examined by using Wootters' criterion [32]. Two probability distributions $\rho^{(1)}$ and $\rho^{(2)}$ are distinguishable after L trials ($L \rightarrow \infty$) if and only if $(J(\rho^{(1)}, \rho^{(2)}))^{\frac{1}{2}} > \frac{1}{\sqrt{2L}}$.

The present work is a first step to examine the problem of comparison of probability distributions (for atoms and various models) which is an area well developed in statistics, known as information geometry [33].

III. FORMALISM

The key quantities in our work are the density distribution $\rho(\mathbf{r})$ and the momentum distribution $n(\mathbf{k})$. In general the calculation of $\rho(\mathbf{r})$ and $n(\mathbf{k})$ presuppose the knowledge of the one body density matrix $\rho(\mathbf{r}_1, \mathbf{r}'_1)$ which is defined as

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) \Psi(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) d\mathbf{r}_2 \dots d\mathbf{r}_Z \quad (24)$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ is the wave function that describes the system under consideration (in the present work the atom). $\rho(\mathbf{r})$ is just the diagonal part of the $\rho(\mathbf{r}_1, \mathbf{r}'_1)$, i.e.

$$\rho(\mathbf{r}_1) = \rho(\mathbf{r}_1, \mathbf{r}'_1)|_{\mathbf{r}_1=\mathbf{r}'_1}$$

while $n(\mathbf{k})$ is the Fourier transform of the one-body density matrix i.e.

$$n(\mathbf{k}) = \int \rho(\mathbf{r}_1, \mathbf{r}'_1) \exp[-i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}'_1)] d\mathbf{r}'_1 d\mathbf{r}_1$$

In the framework of the Hartree-Fock approximation, which is applied in the present work, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ has the well known form of a Slater determinant (electrons of the atoms consist a system which obeys the Fermi-Dirac statistics). It is easy to prove that in that

case $\rho(\mathbf{r}_1, \mathbf{r}'_1)$ takes the following simple form

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = \sum_i \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}'_1) \quad (25)$$

where $\phi_i(\mathbf{r})$ is the single particle wave function describing the electrons in an atom. The index i runs over all Z single particle states. Now $\rho(\mathbf{r})$ and $n(\mathbf{k})$ are written as

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \quad (26)$$

$$n(\mathbf{k}) = \sum_i \tilde{\phi}_i^*(\mathbf{k}) \tilde{\phi}_i(\mathbf{k}) \quad (27)$$

where

$$\tilde{\phi}_i(\mathbf{k}) = \int e^{-i\mathbf{k}\mathbf{r}} \phi_i(\mathbf{r}) d\mathbf{r} \quad (28)$$

The wave functions $\phi_i(\mathbf{r})$ and $\tilde{\phi}_i(\mathbf{k})$ are decomposed in the usual form

$$\phi_i(\mathbf{r}) = \phi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\Omega_r)$$

and

$$\tilde{\phi}_i(\mathbf{k}) = \tilde{\phi}_{nlm}(\mathbf{k}) = \tilde{R}_{nl}(k) Y_{lm}(\Omega_k)$$

The radial momentum wave function $\tilde{R}_{nl}(k)$ is related to the radial wave function in coordinate space through

$$\tilde{R}_{nl}(k) = 4\pi \int_0^\infty r^2 R_{nl}(r) j_l(kr) dr \quad (29)$$

where $j_l(kr)$ is a spherical Bessel function.

In the present work we consider very accurate spin-independent atomic wave functions obtained by Bunge *et al* [19] by applying the Roothaan-Hartree-Fock method to calculate analytical self-consistent-field atomic wave function. In this approach the radial atomic orbitals R_{nl} are expanded as a finite superposition of primitive radial functions

$$R_{nl}(r) = \sum_j C_{jnl} S_{jl}(r) \quad (30)$$

where the normalized primitive basis $S_{jl}(r)$ is taken as a Slater-type orbital set,

$$S_{jl}(r) = N_{jl} r^{n_{jl}-1} e^{-Z_{jl}r} \quad (31)$$

where the normalization factor N_{jl} is given by

$$N_{jl} = (2Z_{jl})^{(n_{jl}+1/2)} / [(2n_{jl})!]^{1/2} \quad (32)$$

and n_{jl} is the principal quantum number, Z_{jl} is the orbital exponent, and l is the azimuthal quantum number.

In general $\rho(\mathbf{r})$ is not spherically symmetric and depends in addition on the angle θ . In the present work we consider $\rho(\mathbf{r})$ averaged spherically (the same holds also for $n(\mathbf{k})$).

The Shannon information entropy in position-space, momentum space and in total are given in Eqs. (2), (3) and (4) respectively.

Another quantity which gives information about the localization (delocalization) of the atomic systems is the local Shannon entropy defined (in position- and momentum-space respectively) as follows

$$\begin{aligned} S_r^{LOC}(\mathbf{r}) &= -4\pi r^2 \rho(\mathbf{r}) \ln \rho(\mathbf{r}) \\ S_k^{LOC}(\mathbf{k}) &= -4\pi k^2 n(\mathbf{k}) \ln n(\mathbf{k}) \end{aligned} \quad (33)$$

In order to formulate the concept of the similarity or information distance between two atomic systems with $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ the corresponding density distributions, the Kullback-Leibler relative entropy is defined as

$$K = \int \rho_A(\mathbf{r}) \ln \frac{\rho_A(\mathbf{r})}{\rho_B(\mathbf{r})} d\mathbf{r} \quad (34)$$

which may be interpreted as a measure of deviation of $\rho_A(\mathbf{r})$ from $\rho_B(\mathbf{r})$. The corresponding symmetrized Kullback distance SK is

$$SK = \int \rho_A(\mathbf{r}) \ln \frac{\rho_A(\mathbf{r})}{\rho_B(\mathbf{r})} d\mathbf{r} + \int \rho_B(\mathbf{r}) \ln \frac{\rho_B(\mathbf{r})}{\rho_A(\mathbf{r})} d\mathbf{r} \quad (35)$$

The physical meaning of the Kullback distance is very clear. K is equal to zero for two identical species and approaches infinity as the difference between $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ increases. K and SK in momentum space are defined using $n_A(\mathbf{k})$ and $n_B(\mathbf{k})$ in the same way.

The Jensen-Shannon divergence entropy is defined as follows

$$\begin{aligned} J &= - \int \left(\frac{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})}{2} \right) \ln \left(\frac{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})}{2} \right) d\mathbf{r} \\ &+ \frac{1}{2} \int \rho_A(\mathbf{r}) \ln \rho_A(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho_B(\mathbf{r}) \ln \rho_B(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (36)$$

The physical meaning of J is similar to SK , while the definition in momentum space is defined using $n(\mathbf{k})$ in the same way.

Another aspect of our work is to compare RHF densities with those of the work [35] in the framework of the SK and J . More specifically we compare the density distributions of the electrons originating from the paper of Bunge et.al. [19] (used in the present work) with the phenomenological one of Sagar et.al. [35] who employed the phenomenological form

$$\rho(r) = \frac{(2I_1)^{3/2}}{\pi} e^{-2(2I_1)^{1/2}r} \quad (37)$$

where I_1 is the first ionization potential of the system. We also compare RHF densities with those of the well known Thomas-Fermi model. For the density distribution we use the simple form obtained by Sommerfeld [36] where

$$\rho(r) = C_{norm} \frac{2^{3/2} Z^{3/2}}{3\pi^2 r^{3/2}} \left(1 + \left(\frac{r}{\mu\alpha} \right)^d \right)^{-\frac{3}{2}c} \quad (38)$$

where $\alpha = 12^{2/3}$, $d = 0.772$, $c = 3.886$ and $\mu = 0.885341/Z^{1/3}$. The normalization constant C_{norm} is calculated from the normalization condition $\int \rho(\mathbf{r}) d\mathbf{r} = 1$

IV. NUMERICAL RESULTS AND DISCUSSION

In Fig. 1 (a) and (b) we plot the Shannon information entropy both in coordinate-space (S_r) and momentum-space (S_k) as functions of the electron number Z . In S_r coexist an average increasing behavior and also an obvious shell effect structure around fully filled shells, such as He, Ne, Ar, Kr where there are minima of the curve $S_r(Z)$. The physical meaning of that behavior is that $\rho(r)$ for these atoms is the most compact one when compared to the neighboring atoms. The values of S_k (Fig. 1 (b)) show a monotonic increase with Z . However there is also in the behavior of S_k a local shell effect.

In Fig. 2 (a) we plot the total Shannon information entropy S . S is a strictly monotonic increasing function of Z with only two exceptions for Ni and Pd. These exceptions are due to the fact that S_r and S_k depend on the arrangement of the electrons in shells. There is a delicate balance between S_r and S_k resulting in the general rule that $S = S_r + S_k$ is a monotonic increasing function of Z except in Ni and Pd where the electron arrangement in shells is such that the decrease of the value of S_r cannot be balanced by a corresponding increase of S_k . Thus the monotonicity of S is slightly violated. A shell effect is also obvious

in the behavior of S i.e. minima at closed shells. Fig. 2 (b) illustrates the trend of S as a function of $\ln Z$. The best linear fit is also plotted in the same figure where $S = 6.257 + 1.069 \ln Z$. It is noted that this result is not new but has been already obtained using other wave functions in [7, 8]. In the present work we verify this result with RHF electron wave functions [19] and we employ this framework for new calculations.

In Fig. 3 (a), (b), (c), (d) we plot the complexity measure $\Gamma_{\alpha,\beta}$ in atoms for various values of parameters α and β . It is seen that for all sets of α and β , $\Gamma_{\alpha,\beta}$ shows qualitatively the same trend as function of Z i.e. it fluctuates around an average value and shows local minima for atoms with closed shells. These results compare favorably with intuition i.e. complexity is less at closed shells which can be considered more compact than neighboring nuclei and consequently less complex. It is noted that this result comes from a procedure which is not trivial i.e. first we calculate $\rho(\mathbf{r})$ and $n(\mathbf{k})$, second we find $S = S_r + S_k$ from the Shannon definition and S_{max} employing rigorous inequalities and third we obtain the complexity measure introduced in [21].

Fig. 4 (a) displays the values of the Onicescu information content O versus Z . The first three maxima correspond to the fully closed shells (He, Ne and Ar) where in the case of the next closed shell (Kr) a local maximum exists. In Fig. 4 (b) we plot in the same footing the Onicescu information content O and the ionization potential I_1 . It is indicated that O and I_1 are correlated in the sense that there is a similarity in the trend of values of O and I_1 as functions of Z . This similarity is more obvious in regions of small Z where linear relations $O = a + b \ln Z$ can be extracted for regions Li-Ne and Na-Ar. However, it seems that, there is no universal relation between them. There are many entropic measures of spread of probability densities e.g. S , E e.t.c. but researchers prefer S because of its unique properties, while E was introduced by Onicescu as a sensitive measure of information. However, S and E are different functionals of the density and their relation is difficult to find.

In Fig. 5 (a) we display the symmetrized Kullback distance between the RHF density distributions and the approximate one given by the relation (37). It is obvious that the symmetrized Kullback distance SK becomes minimum in the case of the fully closed shells atoms. This physically means that the approximate $\rho(\mathbf{r})$ (37) works better in closed shell atoms than the open shells. In addition there is an increasing trend with Z . That means that in general $\rho(\mathbf{r})$ (37) fails to describe the structure of heavier atoms. Fig. 5 (b) displays the Jensen-Shannon divergence entropy J as a function of Z . The behavior is almost similar

to SK and the comments are the same. In Fig. 5 (c) we display J versus SK . There is a linear relation of the two information distances.

In Fig. 6 (a) we display SK as an information distance between the RHF density distribution and the Thomas-Fermi density distribution given by the relation (38). It is seen that the values of SK decrease with Z . This is expected because the Thomas-Fermi approximation works well in heavier atoms. So the two distributions are closer in heavier atoms than in the light ones. The local maxima of the values of SK correspond to the closed shell atoms. This deviation is due to the absence of shell effect character of the Thomas-Fermi distribution compared to the realistic RHF density distribution. Fig. 6 (b) displays J as a function of Z . The behavior is almost similar to SK . In Fig. 6 (c) we display J versus SK .

The local Shannon entropy (33) both in position- and momentum-space is presented in Fig. 7 for various atoms. As it is pointed out in [37] in systems with density $\rho(\mathbf{r}) > 1$ near the nucleus the local Shannon entropy in position-space S_r^{LOC} will be negative, thus the contribution to the integral from this region will serve to lower its value (localization) while in region where $\rho(\mathbf{r}) < 1$, such as the valence, contribution to the Shannon entropy in position-space will be positive which leads to delocalization. In contrast the local Shannon entropy in momentum-space S_k^{LOC} is always positive. This is due to the fact that $n(\mathbf{k}) < 1$ for all k . So, there is no negative contribution to the Shannon entropy in momentum-space.

It is worth, discussing the behavior of the momentum distribution and as a consequence the local Shannon entropy, to mention that the precise knowledge of the electron momentum distribution is important for atoms used as a dark matter or neutrino detectors. In such a kind of experiments the single particle wave function in momentum space or in general the momentum density of the electrons are the main ingredient of the relative cross sections. The trend (localization, delocalization, etc) of the electron wave function or momentum distribution affect considerably the values of the cross sections, especially in experiments where the production of electrons in neutralino-nucleus or neutrino-nucleus collisions are investigated [38, 39, 40].

Finally in Table I we tabulate for the sake of reference the quantities S_r , S_k , S , S_{max} , Ω , and O for each atom as functions of Z . We include the results for Hydrogen which are known exactly i.e. $S_r = 3 + \ln \pi$ and $S_k = \ln 32\pi^2 - \frac{10}{3}$.

V. SUMMARY

In previous works the universal relation $S = a + b \ln N$ was proposed for the information entropy S as function of the number of particles N in atoms, nuclei, atomic clusters and correlated bosons in a trap i.e. systems of various sizes, with various interactions, obeying different statistics (fermions and bosons). In this paper we verify the above relation employing RHF electron density distributions for atoms. Thus we construct a basis in order to study some information-theoretic properties of atoms. Specifically, we calculate the symmetrized Kullback-Leibler relative entropy SK and the Jensen-Shannon divergence J which serve as measures of information distance of probabilities distributions and are useful to compare electron distributions according to various models. Two examples are given. We compare RHF density distributions first with an asymptotic density depending on the ionization potential and second with the well-known Thomas Fermi approximation.

We also obtain Onicescu's information energy E and its corresponding information measure, which correlates with the ionization potential. Finally, we calculate a recently proposed complexity measure $\Gamma_{\alpha,\beta}$ inspired by Landsberg's order parameter Ω . It turns out that the function $\Gamma_{\alpha,\beta}(Z)$ shows the interesting feature that for closed shells atoms is smaller than neighboring ones. This indicates that closed shells atoms are less complex than neighboring ones, which compares favorably with expectations according to intuition.

VI. FINAL COMMENTS

There is a long debate in the literature on order, disorder, complexity and organization for physical, biological and other systems. A generally accepted quantitative definition of complexity does not exist so far. More work has been carried out in classical systems and much less in quantum ones. Our aim is to contribute in this debate examining complexity in atoms (for the first time to our knowledge) adopting a particular definition of complexity measure according to Shiner, Davison and Landsberg [21]. The reason for our choice is that we can easily calculate it for atoms (and we intend to calculate it for other quantum systems as well), because our previous experience with information entropy facilitates this. More work is needed in the future by using the so called statistical measure of complexity of Lopez-Ruiz, Manchini and Calbet [41]

In [42] the authors studied disorder and complexity in an ideal Fermi gas of electrons. They observed that for a small number of electrons Landsberg's order parameter Ω is small, while Ω increases as one pumps electrons into the system and the energy levels fill up. This result is in a way counter-intuitive and indicates that as particles are added in a quantum-mechanical system, the system becomes more ordered. This result was further corroborated in [43] by calculating Ω as function of the number of particles N for realistic quantum systems i.e. atomic nuclei and atomic clusters. In [4] $\Omega(N)$ was obtained for bosonic systems as well (correlated atoms in a trap). All cases show the same trend for $\Omega(N)$ i.e. Ω is an increasing function of N . However, if one is interested how complex (or organized) is a system, the information entropy S (sometimes used as a measure of disorder) or the order parameter Ω (or disorder $\Delta = 1 - \Omega$) are not suitable measures of complexity or organization. We note that these terms are interrelated from a semantic point of view. $\Gamma_{\alpha,\beta}$ has the advantage of being a convex measure of order (or disorder) i.e. it vanishes for highly ordered and disordered systems. In other words, it satisfies the "one-hump" criterion for statistical complexity measures. Thus $\Gamma_{\alpha,\beta}$ is obtained by multiplying a measure of "order" by a measure of "disorder". A simple example is a perfect crystal which has perfect order and an ideal gas with complete disorder. Both have zero complexity and fit well with the definition of $\Gamma_{\alpha,\beta}$.

In the present paper we find that complexity is less at closed shell atoms. This satisfies our intuition, at least does not contradict common sense and indicates that our procedure from electron densities to information entropy and maximum entropy to complexity measure $\Gamma_{\alpha,\beta}$ is reasonable. The fact that $\Gamma_{\alpha,\beta}$ fluctuates around an average value is new and interesting, because it shows that complexity of atoms does not increase as the atomic number Z increases. In other words, as one pumps electrons into the atom, the atom has not the ability to grow in complexity. The question is open what happens if atoms form molecules, molecules form more complex systems e.t.c. We mention that the question whether physical or biological systems have the ability for organized complexity without the intervention of an external factor or agent is a hot subject in the community of scientists interested in complexity and can be extrapolated even in philosophical questions.

VII. ACKNOWLEDGMENTS

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TABLE I: The values of various quantities in our systematic study.

Z	Atom	S_r	S_k	S	S_{max}	Ω	O
1	H	4.14473	2.42186	6.56659	7.9054	0.21113	120.26700
2	He	2.69851	3.91342	6.61193	7.0493	0.06204	100.36100
3	Li	3.07144	3.99682	7.69826	10.3578	0.25677	9.15713
4	Be	3.62386	4.19019	7.81405	10.3950	0.24829	8.45434
5	B	3.40545	4.70590	8.11135	10.3738	0.21810	15.96530
6	C	3.10602	5.15658	8.26260	10.2624	0.19492	25.71210
7	N	2.80169	5.54934	8.35103	10.1520	0.17740	37.43200
8	O	2.55054	5.86737	8.41791	10.1113	0.16747	48.48340
9	F	2.29883	6.16333	8.46215	10.0533	0.15827	61.14500
10	Ne	2.05514	6.43707	8.49221	9.9908	0.14999	75.24470
11	Na	2.33009	6.48310	8.81319	11.6463	0.24326	15.86900
12	Mg	2.39540	6.51440	8.91038	11.8296	0.24677	10.19480
13	Al	2.44569	6.61928	9.06497	12.0615	0.24843	12.76590
14	Si	2.41914	6.73380	9.15294	12.0500	0.24042	15.63600
15	P	2.35903	6.84865	9.20767	11.9954	0.23240	18.62490
16	S	2.29932	6.94939	9.24871	11.9769	0.22779	20.80380
17	Cl	2.22174	7.05243	9.27418	11.9315	0.22716	23.36830
18	Ar	2.13383	7.15541	9.28924	11.8758	0.21780	26.21000
19	K	2.30177	7.17242	9.47419	12.9220	0.26682	10.37540
20	Ca	2.36309	7.18250	9.54334	13.0994	0.27147	6.66998
21	Sc	2.29814	7.30329	9.60143	13.0334	0.26332	8.12090
22	Ti	2.21855	7.42693	9.64548	12.9721	0.25644	9.48793
23	V	2.13512	7.54717	9.68229	12.9160	0.25036	10.91540
24	Cr	1.95589	7.75135	9.70724	12.5913	0.22905	27.02960
25	Mn	1.96257	7.77688	9.73945	12.8162	0.24007	13.94220
26	Fe	1.88213	7.88265	9.76478	12.7697	0.23532	15.78050

27 Co	1.80001	7.98612	9.78613	12.7264	0.23104	17.65210
28 Ni	1.71826	7.99294	9.71120	12.7198	0.23653	18.83670
29 Cu	1.56325	8.25076	9.81401	12.4646	0.21265	41.47510
30 Zn	1.55625	8.27867	9.83493	12.6106	0.22011	23.74300
31 Ga	1.57444	8.32388	9.89832	12.8676	0.23076	23.52780
32 Ge	1.56746	8.37150	9.93896	12.9098	0.23012	24.53250
33 As	1.54980	8.41828	9.96808	12.9082	0.22777	25.68280
34 Se	1.53425	8.45851	9.99276	12.9298	0.22715	25.81220
35 Br	1.51064	8.49958	10.01020	12.9230	0.22540	26.44050
36 Kr	1.48146	8.54092	10.02240	12.9026	0.22323	27.33700
37 Rb	1.57626	8.54430	10.12060	13.7376	0.26329	12.45970
38 Sr	1.62144	8.54228	10.16370	13.9159	0.26963	7.91895
39 Y	1.61438	8.59046	10.20480	13.8772	0.26463	9.57134
40 Zr	1.59462	8.64054	10.23520	13.8304	0.25995	10.94010
41 Nb	1.52486	8.73236	10.25720	13.5780	0.24457	23.59820
42 Mo	1.49117	8.78233	10.27350	13.5247	0.24039	25.89550
43 Tc	1.50762	8.79074	10.29840	13.7087	0.24877	14.73730
44 Ru	1.40305	8.87561	10.30610	13.4876	0.23588	28.97120
45 Rh	1.39635	8.92206	10.31840	13.4670	0.23380	30.46670
46 Pd	1.30482	8.98908	10.29390	13.1570	0.21761	47.72420
47 Ag	1.32346	9.01391	10.33740	13.4264	0.15816	33.39990
48 Cd	1.33132	9.02613	10.35740	13.5464	0.23541	21.51740
49 In	1.35191	9.04892	10.40080	13.7432	0.24320	20.89160
50 Sn	1.35701	9.07295	10.43000	13.7921	0.24377	21.00720
51 Sb	1.35483	9.09683	10.45170	13.8039	0.24285	21.24880
52 Te	1.35345	9.11719	10.47060	13.8313	0.24297	20.80400
53 I	1.34658	9.13832	10.48490	13.8349	0.24214	20.74270
54 Xe	1.33582	9.16022	10.49600	13.8264	0.24087	20.89380

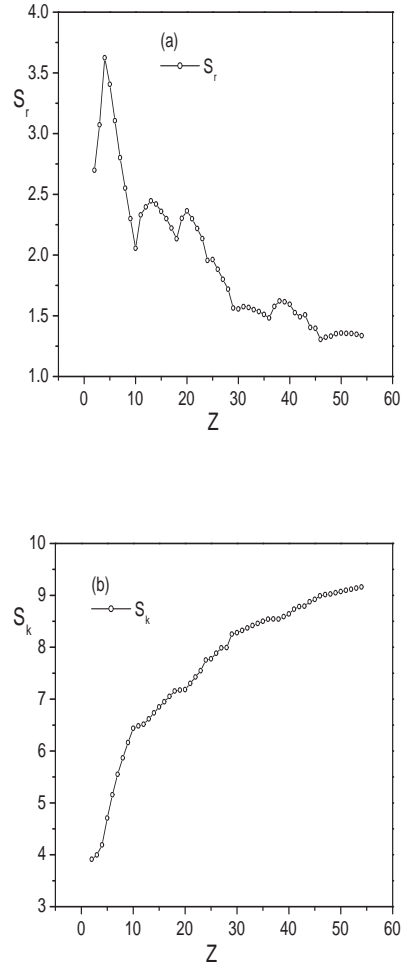


FIG. 1: Shannon information entropy (a) in coordinate-space S_r and (b) in momentum-space S_k , as a function of the electron number Z .

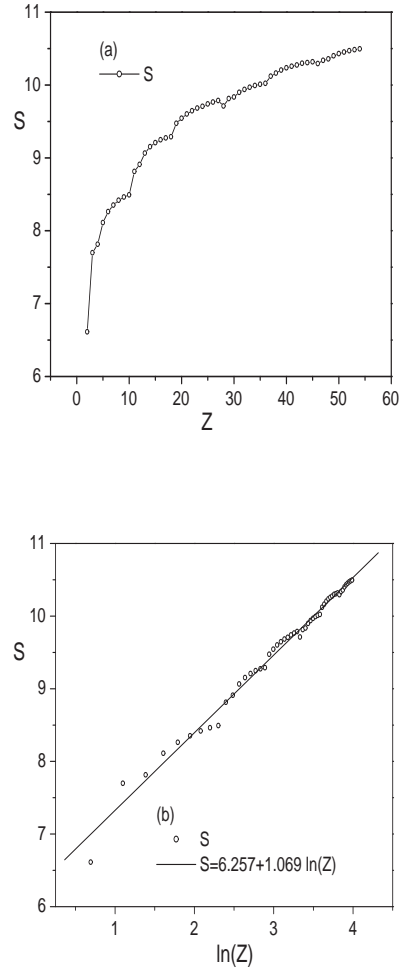


FIG. 2: (a) Total Shannon Information entropy S . (b) S as a function of $\ln Z$ and linear fit.

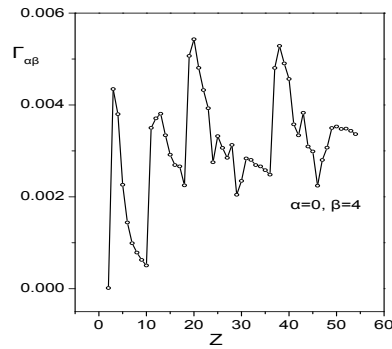
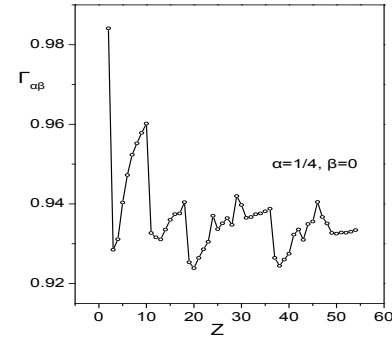
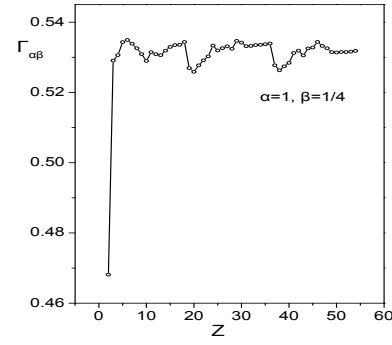
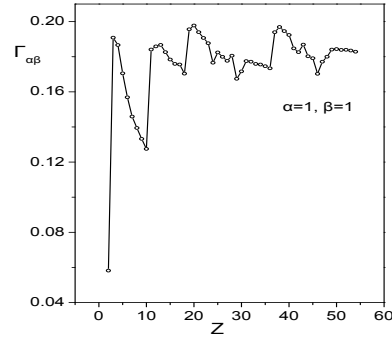


FIG. 3: Complexity measure $\Gamma_{\alpha,\beta}$ for various sets of parameters α and β as a function of Z .

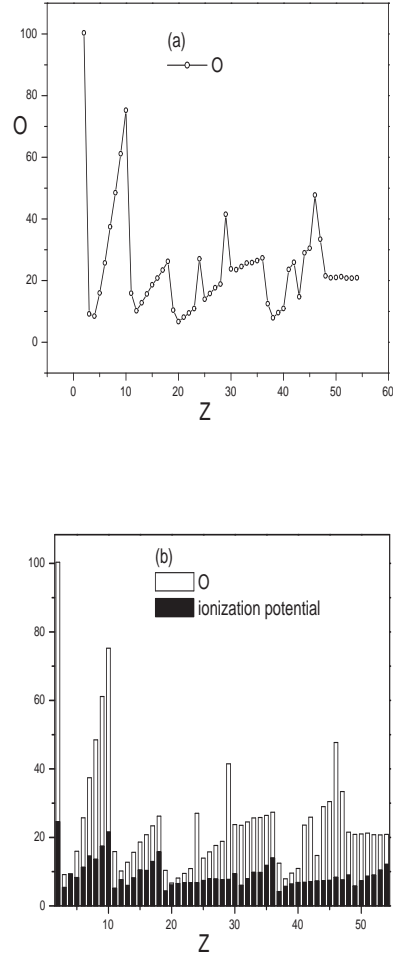


FIG. 4: (a) Onicescu information content O versus Z , (b) Onicescu information content O and ionization potential I_1 (in Hartree units) versus Z .

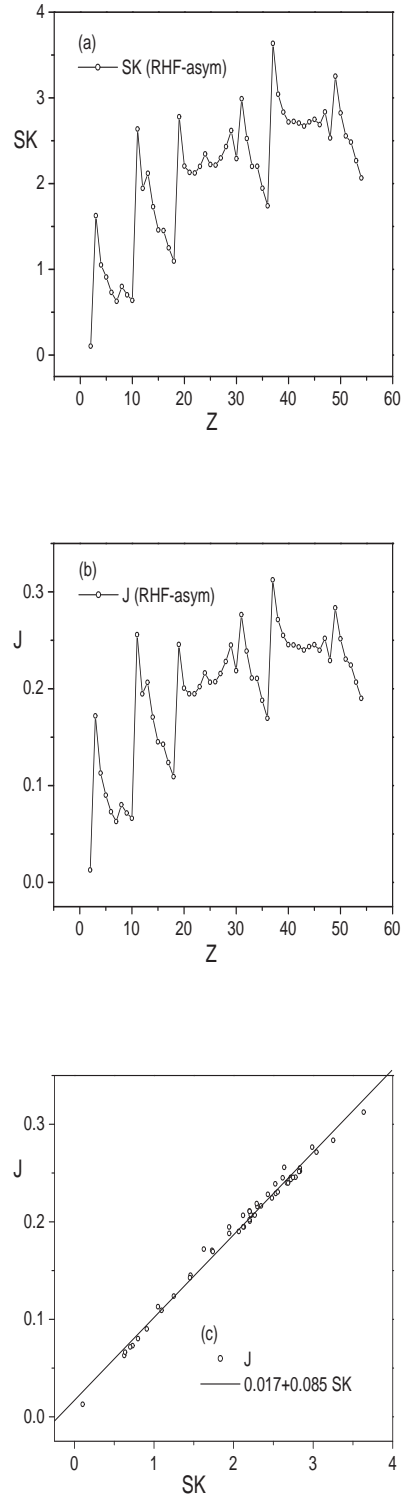


FIG. 5: (a) Symmetrized Kullback distance between the RHF density distribution and the approximate (asymptotic) one (Eq. (37)) (b) corresponding Jensen-Shannon divergence entropy versus Z (c) Jensen-Shannon divergence versus the symmetrized Kullback distance.

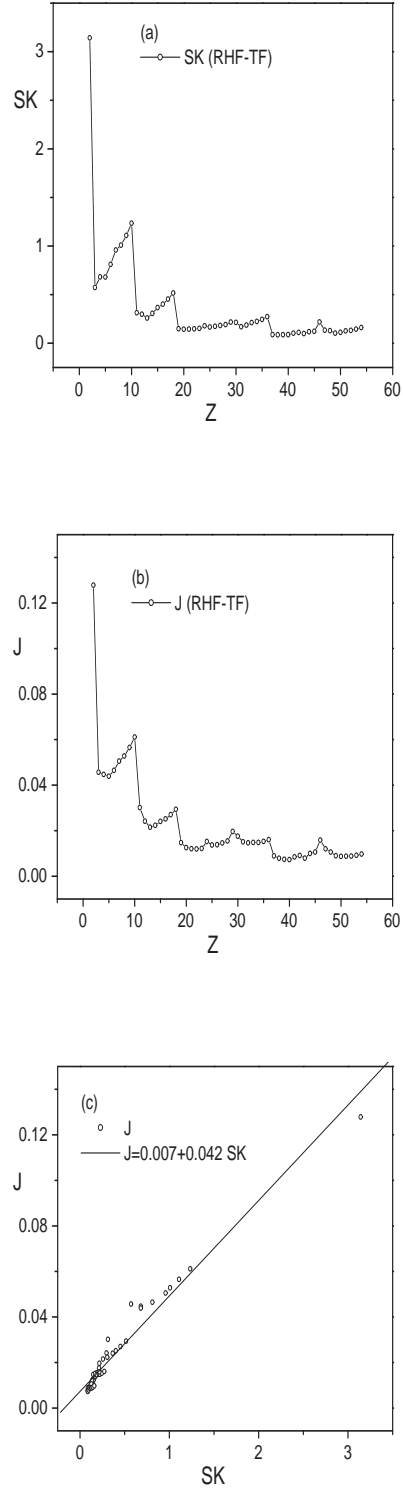


FIG. 6: (a) Symmetrized Kullback distance between the RHF density distribution and the Thomas-Fermi density distribution as functions of Z (b) corresponding Jensen-Shannon divergence entropy versus Z (c) Jensen-Shannon divergence versus the symmetrized Kullback distance.

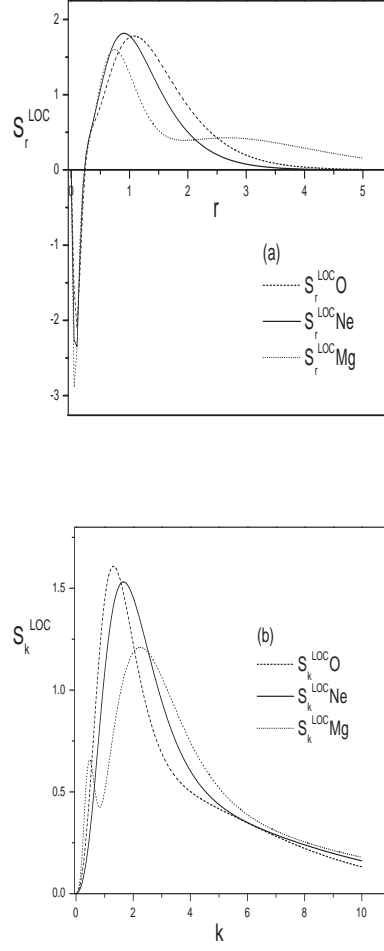


FIG. 7: Local Shannon information entropy (a) in coordinate-space S_r^{LOC} and (b) in momentum-space S_k^{LOC} , as a function of the electron number Z .